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# METHOD FOR MANUFACTURING A POLYTRIMETHYLENE TEREPHTHALATE FIBER

Inventors: Masato Yoshimoto
3-9-233 Mimihara
Ibaraki-shi

Yoshikage Matsui
12-3 Nakatsu-cho
Ibaraki-shi

Applicant: Teijin Co., Ltd.
1-11 Minami-Honmachi
Higashi-ku, Osaka-shi

Agent: Shunichi Hodaka,
patent attorney

1. Title

Method for manufacturing a polytrimethylene terphthalate fiber

2. Claim

A method for manufacturing a polytrimethylene terephthalate fiber with the following characteristics: polymethylene terephthalate wherein at least 85 mol% of repeating units consist of trimethylene units is melt-spun at a spinning rate of 2000 m/min or above for the purpose of producing an unstretched yarn with an index of bifringence $\Delta n$ of 0.035 or above, and the unstretched yarn is subsequently stretched with a preheating roller whose temperature is controlled at 35-80°C.

3. Detailed explanation of the invention

The present invention concerns a method for manufacturing a polytrimethylene terephthalate fiber. More specifically, the present invention concerns a method for manufacturing a polytrimethylene terephthalate fiber in a stable state free from laps, fluffs, cut yarns, etc.

Polyethylene terephthalate fibers are the mainstream of synthetic fibers today, and there are numerous production techniques. Moreover, polybutylene terephthalate fibers have also been used for various purposes in recent years, and many production methods have been noted.

On the other hand, there has been hardly any research on polytrimethylene terephthalate fiber, which holds an intermediate state between polyethylene terephthalate and polybutylene terephthalate in the number of methylene groups.

The polytrimethylene terephthalate fiber has high elongation, excellent elastic resiliency, low Young's modulus, excellent

dyeing properties, and high chemical stability. Thus, it is an excellent clothing fiber.

However, when an oridinary spinning method is employed for producing a trimethylene [sic] terephthalate fiber, the orientation and crystallinity of an unstretched yarn are extremely low. Moreover, since the glass transition point is as low as 35°C, the properties of the raw yarn change drastically over time. For example, since the primary yield stress, natural elongation, and maximum elongation change by the hour, it is extremely difficult to carry out a successful stretching operation. Moreover, it is difficult to carry out a stable production because of significant fluffs, laps, and cut yarns.

In response to these problems, the present inventors compiled exhaustive research on a method for consistently producing a polytrimethylene terephthalate fiber without causing fluffs, laps, and cut yarns. As a result, the present invention has been completed.

Put succinctly, the present invention concerns a method for manufacturing a polytrimethylene terephthalate fiber with the following characteristics: polytrimethylene terephthalate wherein at least 85 mol% of repeating units consist of trimethylene units is melt-spun at a spinning rate of 2000 m/min or above for the purpose of producing an unstretched yarn with an index of birefringence $\Delta n$ of 0.035 or above, and the unstretched yarn is subsequently stretched with a preheating roller whose temperature is controlled at 35-80°C.

In the paragraphs to follow, the present invention will be explained in great detail.

The polytrimethylene terephthalate of the present invention may contain less than 15 mol% of a third component so long as at least 85 mol% of the repeating units are trimethylene terephthalate units.

Polytrimethylene terephthalate can be synthesized by reacting and bonding terephthalic acid or its functional derivatives and triethylene glycol and its functional derivatives in the presence of a catalyst under the proper set of conditions. One, two, or more third components may be added prior to the completion of the polymerization of polytrimethylene terephthalate for the purpose of producing a copolymerized polyester. Specific examples of third components include: aliphatic dicarboxylic acids containing two ester-forming functional groups, alicyclic dicarboxylic acids, aromatic dicarboxylic acids, oxycarboxylic acids, and their functional derivatives. Moreover, the polytrimethylene terephthalate may contain delustering agents (e.g., titanium dioxide, etc.), stabilizers (e.g., phosphoric acid, phosphorus acid, their esters, etc.), ultraviolet absorbents (e.g., hydroxybenzophenone derivatives, cyanoacrylate derivatives, etc.), flame retardants, electrical control agents, etc.

Moreover, it is desirable that the aforementioned polytrimethylene terephthalate have a limiting viscosity [η] of 0.50-1.20, preferably 0.65 to 1.10. If the limiting viscosity is below 0.50, the melt viscosity of the polymer is too low, which adversely affects spinning stability, and the strength of the resulting fiber is only marginal. On the other hand, if the limiting viscosity exceeds 1.20, the melt viscosity is too high, and it

is difficult to carry out a smooth measurement with a gear pump. Moreover, spinning properties are reduced due to poor extrusion.

The limiting viscosity [η] is a value calculated with the following difinitional equation:

$$[\eta] = \lim_{C \to 0} \frac{1}{C} (\eta_r - 1)$$

(wherein $\eta_r$ is a value obtained by dividing the viscosity of a dilute o-chlorophenol solution containing polytrimethylene terephthalate (purity: at least 98%) with the viscosity of the intrinsic viscosity of the aforementioned solvent at the same temperature and by using identical units. It is oftentimes referred to as the relative viscosity. C is the weight of soluble matters in 100 cc of the aforementioned solution (unit: gram)).

When the aforementioned polytrimethylene terephthalate is melt-spun, it is desirable that the spinning temperature be maintained at 245 to 290°C, preferably 260 to 280°C. If the spinning temperature is below 245°C, it is difficult to attain a stable molten state since the temperature is too low, and the resulting fiber fails to exhibit adequate strength and elongation. On the other hand, if the spinning temperature exceeds 290°C, it is undesirable since the fiber is significantly pyrolyzed.

When the method of the present invention is implemented, the spinning rate is set at 2000 m/min or above, preferably 2500 m/min or above. If the spinning rate is below 2000 m/min, the orientation and crystallinity of the resulting unstretched yarn are extremely low, and due to this unstable state, it is impossible to carry out a smooth stretching procedure. In other words, if the spinning rate is below 2000 m/min, the index of birefringence $\Delta n$, which indicates the degree of orientation of an unstretched yarn, drops below 0.035, and the crystallinity is below 10%. Moreover, since the glass transition point of the polymer is as low as 35°C, molecular movements occur easily even at room temperature, and the properties of the unstretched yarn vary significantly over time. Thus, since significant fluffs and laps are produced during elongation, it is impossible to obtain a polytrimethylene terephthalate fiber with excellent properties.

The index of birefringence is a value inferred from the retardation of polarized beams observed on the surface of a fiber by using a general-purpose optical microscope and a compensator. Crystallinity is calculated as follows: the integral value of interference intensity attributed to a crystal ($2\theta$ = 10-40°) is inferred from the difference between an interference intensity curve obtained by rotating a sample on a place perpendicular to X-rays and an interference curve attributed to a noncrystalline zone connecting the interference valley in the meridian direction is first calculated, and its proportion to the total area after a noninterference disturbance correction is subsequently calculated.

When the unstretched polytrimethylene terephthalate fiber thus spun is stretched, the temperature of a preheating elongation roller exerts tremendous effects on the extent of elongation and the physical properties of the stretched yarn. As far as the present invention is concerned, the temperature of the preheating roller is maintained at 35-80°C, preferably 50-70°C, for elongation. If the temperature of the preheating roller is below 35°C, the strength and elongation of the resulting fiber are marginal, and when the fiber is stretched, significant laps and fluffs are produced. This problem may be accounted for as follows. The unstretched polytrimethylene terephthalate yarn exists in the so-called "shrunk" state, where the repeating unit length of the trimethylene terephthalate is short. Therefore, if the temperature of the preheating roller is below 35°C, preheating is insufficient, and it is difficult to smoothly stretch and orient molecular chains during the elongation procedure. On the other hand, if the temperature of the preheating roller exceeds 80°C, the yarn is easily entangled with the preheating roller during the elongation procedure, and as a result, elongation is reduced. This problem may be accounted for as follows. Since the preheating temperature is too high, polytrimethylene terephthalate is crystallized, accompanied by a reduced elongation, or since molecular movements are intense, the elongation is reduced. As for stretching conditions other than the temperature of the preheating roller, procedures identical to those in the case of common polyester yarn may be used.

In the paragraphs to follow, the method of the present invention will be explained with reference to application examples.

Application Example 1

Polytrimethylene terephthalate (limiting viscosity: 0.90) was melt-spun at a spinning temperature of 280°C, extrusion rate of 36.5 g/min, spinning rate of 3500 m/min, and a cool air-feeding rate of 1.8 $Nm^3$/min. As a result, an unstretched yarn (94 denier/36 filament) was obtained.

The index of birefringence and crystallinity of the resulting unstretched yarn were measured according to the aforementioned methods, and the results were: $\Delta n = 0.075$ and $X_c = 30\%$. Thus, the yarn was sufficiently oriented and crystallized. Next, the resulting unstretched yarn was stretched by turning a heating roller (diameter: 90 mm) which had been heated at 60°C for a total of 8 times. After the unstretched yarn had been stretched at a rate of 500 m/min, a stretched yarn (75 denier/36 filament) was obtained. The elongation state was quite excellent. No laps, cut yarns, or fluffs were produced in a 12-cone simultaneous elongation.

An identical unstretched yarn was left unattended at room temperature (i.e., 20°C) and at a humidity of 60% for 24 hours prior to elongation. The elongation was comparable.

The resulting stretched yarn exhibited a strength of 3.3 g/d, elongation of 38%, and an elastic resiliency of 95% at 10% elongation.

The stretched yarn was temporarily twisted. The processing was smoothly carried out, unaccompanied by cut yarns.

Comparative example

A polytrimethylene terephthalate starter identical to that employed in Application Example 1 was spun under conditions identical to those in Application Example 1 except that the extrusion rate and spinning rate were changed to 26.5 g/min and 1200 m/min, respectively. As a result, an unstretched yarn (198 denier/36 filament) was obtained. The index of birefringence and crystallinity of the resulting unstretched yarn were measured. The results were:

$\Delta n = 0.010$

$X_c < 10\ \%$

(measurement impossible)

Thus, the yarn was hardly oriented or crystallized.

Next, the resulting unstretched yarn was turned 8 times around a hot roller (diameter: 90 mm) which had been heated at 60°C. After it had been stretched at a magnification of 2.65X and elongation rate of 500 m/min, a stretched yarn (75 denier/36 filament) was obtained. The elongation state was extremely poor. In a 12-cone simultaneous elongation treatment, all the cones were plagued with laps and fluffs.

The resulting stretched yarn exhibited the following physical properties: strength: 3.2 g/d; elongation: 37%.

Since the entire stretched yarn was plagued with fluffs, when it was temporarily twisted, fluffs and cut yarns were produced. Thus, it was impossible to obtain an adequate processed yarn.

The forementioned unstretched yarn was left unattended at room temperature (i.e., 20°C) and at a humidity of 60% for 8 hours and then stretched under conditions identical to those of the aforementioned case. As a result, laps and cut yarns were significant, and it was almost impossible to even collect the stretched yarn.

Application Example 2

An unstretched yarn identical to that obtained in the method of Application Example 1 was stretched according to the scheme of Application Example 1 at an elongation magnification of 1.25X, elongation rate of 500 m/min, with the temperatures of the preheating roller being set at 30°C, 60°C, and 85°C. The elongation states and physical properties of stretched yarns are shown in the following table.

| Preheating roller temperature (℃) | Elongation states | | Physical properties of stretched yarn. | |
|---|---|---|---|---|
| | Entanglement with hot roller | Laps | Strength (g/d) | Elongation |
| 30 | ○ | × | 2.7 | 32 |
| 60 | ○ | ○ | 3.3 | 37 |
| 85 | × | △ | 3.0 | 38 |

In the table, the category "entanglement with hot roller" indicates a frequency by which cut yarns are produced due to the entanglement of an unstretched yarn with the hot roller. X indicates a high frequency (1 cut yarn in 5 to 20 minutes), and O indicates a virtual absence of entanglement and cut yarns. The category of "laps" indicates the entanglement of a fiber with the elongation roller between hot rollers. X indicates a high frequency (1 lap in 10 to 15 minutes). Δ indicates a medium frequency (1 lap in 15 to 30 minutes). O indicates that 1 kg of a stretched yarn was completely wound and collected after a stable elongation unaccompanied by the production of laps.

As the results of the table clearly indicate, when a polytrimethylene terephthalate fiber is stretched, the temperature of an elongation preheating roller (i.e., hot roller) exerts a tremendous effect. If the fiber is stretched at a hot roller temperature of 35°C to 80°C, preferably 50°C to 70°C, a stretched yarn equipped with excellent physical properties can be produced in a stable state unaccompanied by cut yarns and fluffs.

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Ralph McElroy Company
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